Volcanic sulfides and outgassing

Marie Edmonds[1] and Tamsin A. Mather[2]

1 Department of Earth Sciences, University of Cambridge

2 Department of Earth Sciences, University of Oxford

Sulfides are a major potential repository for magmatic metals and sulfur. In more reduced magmas, there may be a dynamic interplay between sulfide liquids and degassing as magmas ascend/erupt. Sulfide-bubble aggregates may segregate to shallow levels. Exsolved fluids may oxidize sulfides producing SO_2 gas and metals, which may vent to the atmosphere with chalcophile metal ratios reflecting those in the sulfide liquids. Sulfide breakdown and/or sequestration timing and balance define the role of sulfides in both ore formation and the environmental impacts of volcanic eruptions, including during Large Igneous Provinces, key periods of heightened volcanism during Earth history.

Key words: sulfide, outgassing, metals, partitioning, vapor, eruptions

INTRODUCTION

Sulfides are a common feature of near surface magmas (**figure 1**) and play an important role in volcanic systems in the supply of sulfur and chalcophile metals to the atmosphere and to sites of ore formation. Sulfur is one of the most abundant and important volatile species produced by volcanic activity. Volcanic eruptions may produce large clouds of sulfur dioxide which, when injected into the stratosphere, convert to sulfate aerosol and may impact climate by absorbing near-IR radiation and scattering it back into space. Tropospheric plumes of sulfur gases and aerosol may be large enough to cause environmental damage and health hazards. Sulfur-rich

fluids at submarine mid-ocean ridges, formed by the outgassing of ascending basaltic melts, support sulfide-oxidising microbial life and modulate ocean chemistry and oxidation state.

Sulfur is a ubiquitous component of magmas and displays complex behavior due to its ability to exist in many valence states and species (S^{2-}, S^{6+}, S^0 and as S_2, SO_2, SO_3 and H_2S in the gas phase). Its behaviour in magmas is largely dependent on magma oxidation state (the availability of oxygen) (Carroll and Rutherford, 1985). Under reduced conditions sulfur dissolves as sulfide (S^{2-}) and under oxidized conditions, as sulfate (S^{6+} in SO_4^{2-}); under intermediate conditions both speciation states are present. Dissolved sulfur species will progressively concentrate in melts during crystallization (of non-sulfur-bearing phases), until eventually, the melt concentration of sulfur may reach the level required for the precipitation of (or "saturation in") a non-volatile, sulfur-bearing phase. The form of this phase is dependent on both the fugacities (or put simply, the abundance or availability) of oxygen and sulfur in the system. Under oxidized conditions, the solid sulfur-bearing phase is anhydrite ($CaSO_4$). In relatively reduced magmas typical of mid-ocean ridges, for example, this sulfur-bearing phase might be monosulfide solid solution (mss) or a Fe-O-S immiscible liquid, which quenches to a sulfide solid solution (Parat et al., 2011). Photomicrographs to show quenched sulfide liquids in a range of volcanic rocks, in the form of inclusions in crystals and in the matrix glass, are shown in **figure 1**.

Sulfide liquids display a range of compositions and may contain appreciable concentrations of metals such as copper (Cu) and nickel (Ni). Sulfide liquids are dense relative to silicate melts and may settle gravitationally and be reworked multiple times, leading to the segregation of massive volcanigenic sulfide deposits (Ripley and Li, 2013), which may have substantial economic value. In volcanic systems, however, which involve magmas stored at low pressures, hydrothermal fluids may also coexist with sulfide-saturated magmas. Interaction between oxidising, water-rich fluids and sulfide liquids may promote an interplay between volcanic outgassing and sulfide

saturation such that sulfides might break down, supplying sulfur directly to the atmosphere (Nadeau et al., 2010). Volcanoes are significant sources of metals to the atmosphere via gas and aerosol phases (Mather et al., 2012); where sulfide saturation occurs, some of these metals may derive directly from sulfide breakdown (Larocque et al., 2000).

Sulfur is also volatile in silicate melts, and partitions strongly into a vapor phase at low pressures in the crust, and sulfide saturation may have a key modulating effect on melt-vapor partitioning. Sulfur partitioning behavior is well understood for a wide range of oxidation states and melt compositions. In general, experiments indicate that sulfur partitions strongly into the gas phase, particularly for more reducing conditions below the sulfate-sulfide transition, caused by the lower solubility of sulfur when it exists as the ion S^{2-} than when it occurs, under more oxidizing conditions, dissolved as sulfate (S^{6+}). Saturation of the melt in sulfide or in anhydrite (at more oxidizing conditions) limits the sulfur concentration in the co-existing gas phase to just a few per cent by volume (Zajacz et al., 2012).

The interplay between and timing of these partitioning processes (between silicate melt, vapor and sulfide) has consequences for outgassing or sequestration in reduced volcanic systems. The range of possible processes involving sulfide saturation and vapor saturation of melts, and their consequences is summarised in **figure 2**. The mass budget of sulfur available for degassing into the atmosphere in volcanic systems is often estimated using the sulfur concentration in melt inclusions (tiny increments of melt trapped in growing crystals), the so-called *petrological method* (Sigurdsson et al., 1985), but only rarely is the sulfur in the sulfide liquid phase taken account of, beyond recognition of sulfide saturation. The timing of sulfide saturation and vapor saturation in volcanic systems is likely critical for determining the extent to which metal-rich sulfides are sequestered; and the magnitude of the sulfur-rich gas cloud outgassed with magma during eruptions. The high degree of wetting of hydrous vapor on sulfide liquid droplets may

render the sulfide liquids buoyant, promoting their involvement in volcanic outgassing processes and preventing sulfide sequestration (Mungall et al., 2015).

In this article we review the controls on sulfide liquid formation in volcanic melts and their compositions; and their potential interaction with hydrothermal-volcanic fluids. We discuss the fundamental role that sulfides play in modulating the transport of sulfur from mantle-derived melts to the crust and into the atmosphere, and the feedbacks related to the formation of sulfide ore deposits associated with these magmas.

SULFIDE SATURATION IN ERUPTING BASALTIC MELTS

For the purposes of this paper we focus on those systems that contain substantial quantities of sulfide in the melt, which correspond to magmas in ocean island (or "hotspot"), mid-ocean ridge (MOR) settings, and some arc (subduction-related) magmas. The concentration of sulfur required to saturate in sulfide is known as the *sulfur concentration at sulfide saturation* (SCSS). The sulfate-dominated volcanic systems are beyond the scope of this paper, but are often characteristic of more evolved magmas and extremely important in volcanic arcs, where anhydrite may modulate the mass of sulfur outgassing into the atmosphere (Masotta et al., 2016).

Sulfide-saturation in mid-ocean ridge basalts (MORB)

We will begin by considering the case of MORB; these are well understood and characterized, and are erupted with an oxygen fugacity that ensures that much of the dissolved sulfur is present as sulfide. The amount of sulfur that a melt can dissolve before saturation with respect to a sulfide phase depends on both melt composition (largely the Fe^{2+} content, with which sulfur forms complexes in the melt) but also temperature and pressure. Various empirical models to

104 describe the SCSS have been proposed (Liu et al., 2007) which take account of complex
105 compositional and intrinsic parameters. A schematic illustration to show how typical mid-ocean
106 ridge basaltic melt may evolve due to fractional crystallization is shown in **figure 3**. Sulfide
107 saturation occurs when the sulfur concentration in the melt intersects the SCSS curve. MORBs
108 are thought to be sulfide-saturated during generation in their mantle source region (Mavrogenes
109 and O'Neill, 1999). The decrease in pressure during magma ascent will result in an increase in
110 the SCSS for anhydrous melts (caused by the larger volume of dissolved sulfur over sulfide) and
111 thus tend to drive the magmas toward under-saturation. MORB data, however, show a correlation
112 between sulfur concentration and decreasing Cu with MgO concentrations (Jenner and O'Neill,
113 2012), consistent with sulfide saturation prior to and during eruption, with Cu partitioning into
114 the sulfide phase. Observations of quenched, rounded sulfide blebs in submarine MORB glasses
115 confirm sulfide saturation. An explanation for crustal, late-stage sulfide liquid saturation might be
116 fractional crystallization, which even after modest amounts (~10%) will tend to drive the liquid
117 towards sulfide saturation (Li and Ripley, 2005). A detailed study of the textures of MORB
118 sulfides show that they are typically exsolved into Ni-rich and Cu-rich regions (**figure 4**). The
119 Ni-rich regions, known as monosulfide solution solutions (mss), are also rich in Co and Re; the
120 Cu-rich regions, known as intermediate sulfide solid solutions (iss) are also enriched in Zn, Cd,
121 Ag, Sn, Te, Bi and Au (Patten et al., 2013).
122
123 Basalts erupted in Iceland also display globules of quenched sulfide liquids in their groundmass
124 (**figure 1**) (Sigmarsson et al., 2013), suggesting that, like typical MORB, they are saturated with
125 a sulfide phase shortly before, during and after eruption, due to both fractional crystallisation
126 (increasing the sulfur concentration in the liquid) and cooling (reducing the SCSS). Models
127 predict that tholeiitic basaltic melts from Iceland will become saturated in a sulfide phase after
128 around 50% crystallization, which is illustrated by data from Hekla volcano (Moune et al., 2007).
129 Hekla melt inclusions follow a trend that predicts that they reach sulfide saturation at melt MgO

contents of around 6.5 wt% MgO, which probably takes place during fractional crystallization in upper crustal magma reservoirs shortly before eruption, thereby forming sulfide liquid globules as observed in erupted rocks (**figure 1**).

It is straightforward then, to demonstrate that MORB and Icelandic melts are sulfide-saturated and that sulfide saturation occurred at a relatively late stage, in response to crystallization. MORBs, however, are typically erupted in water depths of > 1 km, which means that little water degassing takes place from the melt and hence the sulfide liquids are unlikely to be in contact with aqueous magmatic fluids and therefore there is limited opportunity to transfer their sulfur burden to the atmosphere or water column (**figure 2**). However, what would be the consequences of subaerial eruption and outgassing of such sulfide-bearing basalts?

Degassing of sulfide-saturated magmas in a range of tectonic settings

As discussed above, Icelandic melts are sulfide-saturated at a relatively late stage of evolution and in response to crystallization. The very large fluxes of sulfur dioxide loading associated with Icelandic eruptions such as Laki (1783; 122 Tg; (Thordarson and Self, 1993) and the more recent Holuhraun eruption (2014; 8.9 +/- 0.3 Tg; (Gauthier et al., 2016)) testify to the sulfur-rich nature of the basaltic melts ascending into the crust beneath Iceland and to the efficient outgassing of sulfur from melts as they decompress and erupt. The role of sulfides in this sulfur outgassing, and its implications in terms of metal release, is worthy of further detailed consideration.

Most magmatic melts are vapor-saturated from the mid-crust, coexisting with a CO_2-rich vapor phase at depth, which becomes more H_2O-rich closer to the surface. The vapor phase also contains significant quantities of sulfur and halogen species. Magmatic sulfide stability is

extremely sensitive to degassing-induced redox changes in the melt, and to removal through outgassing of exsolved sulfur species, which lowers the fugacity of sulfur in the gas phase and induces sulfide liquid (SL) oxidation and breakdown via a reaction of the form (Berlo et al., 2014):

$$3FeS_{SL} + 2H_2O_{melt,fluid} + 2O_{2melt,fluid} \rightarrow Fe_3O_{4,mt} + 2H_2S_{fluid} + SO_{2\,fluid}$$

This reaction results in the formation of magnetite (mt), which does not hold metals in its structure to the same degree as sulfide, resulting in release of the concentrated metals, as well as H_2S and SO_2, directly into the aqueous fluid bubbles-silicate melt system (illustrated in **figure 4**). This process of metal transfer from the sulfide liquid to the volcanic gas phase has been inferred for a range of volcanoes, including more evolved systems such as Kawah Ijen Volcano (Berlo, et al., 2014) and Merapi Volcano (Nadeau, et al., 2010), both in Indonesia. At Merapi, as well as for the Alumbrera porphyry ore deposit, Argentina (Halter et al., 2002), the metal ratios observed in volcanic gases emitted from the crater have the same ratios of Cu to Au as the sulfides trapped as inclusions inside phenocrysts (Nadeau, et al., 2010). At Kawah Ijen, metal concentrations in melt inclusions, combined with abundances of H_2O, CO_2 and S, were used to reconstruct the presence of a sulfide liquid at depth, which sequestered metals. Breakdown of the sulfide phase resulted in redistribution of metals between metals and fluids before outgassing at the volcanic vents (Berlo, et al., 2014). More generally the distribution of metals in volcanic plumes may provide corroborating evidence for such a sulfide breakdown mechanism (**figure 5**). The volcanic gas and aerosol composition of the plume accompanying a recent Icelandic basaltic eruption shows that it was enriched in metals (Gauthier, et al., 2016), with their distribution mirroring the trend in elemental sulfide-silicate melt partitioning behaviour (**figure 5**). In particular, the enrichment in elements like Re, Se and Te in the volcanic aerosol phase are strongly suggestive of an origin by

sulfide breakdown in the melt owing to their extremely high sulfide-silicate melt partition coefficients (>500; (Brenan, 2015)). Once the sulfide has broken down, there may be some further partitioning between fluid and melt, which is likely to be dependent on the chloride concentration of the fluid, owing to the tendency for metal ions to be complexed with chloride (and perhaps sulfur) in the gas phase.

In fact, the sulfide-silicate melt partition coefficients for many key metals are high (>100; **figure 5**) and it follows that, where erupting melts are sulfide-saturated (as appears to be the case for many basalts in a range of settings), most of these metals (90-99.9%) in the magma will likely be sequestered into the sulfide phase prior to eruption, even for small mass abundances of sulfide. This sulfide phase will break down when an aqueous fluid develops in the melt due to vapor-saturation. The metal-rich gases observed at such volcanoes must therefore in large part be derived from the breakdown of sulfide liquids prior to eruption.

The sulfide liquids themselves are often entirely absent in the volcanic rock products, owing to the efficient and rapid nature of the breakdown process described above, but in some cases sulfide globules are preserved in the matrix glasses or more commonly, as inclusions in phenocrysts, protected from the fluid phase by the crystal host (**figure 1**). It therefore follows that many magmas erupted at the surface have lost a large proportion of the sulfide liquids that were present in the magma prior to degassing due to resorption and oxidation. Additional evidence for this comes from comparisons of sulfide form and distribution within intrusive and volcanic rocks from the Tertiary Bingham and Tintic Districts, Utah. Volcanic rocks (and the porphyries) have two orders of magnitude less sulfide by mass than dykes, which were emplaced at higher pressures where degassing was inhibited. The textures of all of the sulfides in the volcanic rocks and porphyries have been modified extensively by resorption and degassing (**figure 4**). Immiscible liquids crystallized as pyrrhotite and chalcopyrite with declining temperature and

206 pressure, and locally recrystallized to pyrite and an Fe-oxide as they were oxidized. The
207 alteration and preservation textures change from subspherical sulfide blebs near the margins of
208 the quenched (and better preserved) dikes and sills, to partially altered sulfides farther in, to
209 complete absence of sulfides in the vast majority of intrusions and volcanic rocks (except where
210 small sulfides are completely enclosed by phenocrysts). The cooling of these magmas, coupled
211 with the degassing of magmatic volatiles, including sulfur-bearing gases (e.g., H_2S, SO_2), caused
212 resorption and oxidation of magmatic sulfides to occur (Larocque, et al., 2000). It has been
213 estimated that degassing and oxidation probably removed greater than 90% of the original
214 endowment of magmatic sulfides. This example illustrates well why volcanic rocks rarely contain
215 sulfides in the matrix glass; and provides explanation for the low-magmatic sulfide abundances of
216 slowly cooled, extensively degassed, large porphyritic intrusions. Most importantly, this process
217 allows metals and sulfur, under some conditions, to participate in the formation of porphyry
218 deposits and in others, to be outgassed into the atmosphere.
219
220 Sulfides therefore may play a much greater role in supplying sulfur to co-eruptive gas plumes
221 than previously assumed; and it is likely that the commonly used *petrological method* to calculate
222 sulfur outputs from past basaltic eruptions (which uses the difference in sulfur concentration
223 between melt inclusions and degassed matrix) might be improved in many cases by
224 reconstruction of sulfide saturation and a robust mass balance using chalcophile element
225 inventories.
226
227 ***Dynamics of sulfide-aqueous fluid interaction***
228
229 An important question relates to how sulfides remain in suspension in relatively low viscosity
230 basaltic liquids in order to participate in the resorption and oxidation reactions discussed above.
231 Sulfide liquids are dense, and therefore they are predicted to settle out of the liquids by gravity

232 and accumulate in basal zones in the magma chamber, which may later form the loci for
233 economically-viable Ni-Cu-PGE sulfide accumulations as evidenced by abundant examples
234 (Ripley and Li, 2013).
235
236 Recently however, experiments have shown that the contact angle for sulfur-bearing vapor on
237 sulfides is small (i.e. the wettability or the ability of the fluid to maintain contact with the solid
238 surface is high); much smaller than for bubbles nucleating on silicate crystal phases such as
239 olivine, pyroxene or plagioclase (Mungall, et al., 2015). Theoretical calculations also show that it
240 is energetically far more favorable for aqueous bubbles to nucleate on sulfides or on sulfide liquid
241 droplets, to the exclusion of all other phases if sulfides are present, even in small amounts
242 (Mungall, et al., 2015). The effect of the formation of sulfide-bubble "compound drops" on their
243 distribution may be profound. If this process occurs at low pressures, the bulk density of the
244 bubble-sulfide liquid aggregate may be lowered sufficiently to render the sulfide liquid buoyant
245 relative to the silicate melt. This buoyancy allows the sulfide liquid to ascend to the surface with
246 the melt during eruptions, participating in the outgassing process, breaking down and supplying
247 its sulfur and metal loads to the atmosphere (**figure 2**). The timing of vapor and sulfide saturation
248 are potentially critical; if sulfide saturation occurs before the generation of a significant gas
249 fraction, then sulfides may be lost and sequestered gravitationally; if vapor saturation occurs
250 concurrently with (or before) sulfide saturation in the upper crust, then buoyant aggregates may
251 form. The melt viscosity and the timescales of settling are also key.
252
253 **THE ROLE OF SULFIDES IN OUTGASSING ASSOCIATED WITH LARGE IGNEOUS**
254 **PROVINCES (LIPs)**
255
256 Hotspot magmatic systems today in the oceans and on the continents provide an analogue for
257 flood basalt provinces in terms of their sulfur budgets and the role of sulfides in outgassing.

Large igneous province (LIP) emplacement has been associated with severe degradation of the Earth's surface environment and also occurs coincident with extreme mass extinctions in the sedimentary record, suggesting a causal link. The potential role of sulfides in LIP degassing has implications in terms of our understanding of these key events in Earth history.

The sulfur budgets of LIPs are notoriously difficult to reconstruct, owing to melt inclusions being commonly small and entirely recrystallized, with some rare exceptions (Self et al., 2008). It is commonly believed that LIP basalts are sulfide-saturated, and in fact this forms the basis of a widely used method to calculate the likely sulfur outgassing budgets of these eruptions, using the MORB FeO-S relationship to estimate the pre-eruptive dissolved sulfur concentration and then applying the petrological method (Blake et al., 2010).

Abundant evidence of sulfide saturation and accumulation exists in large igneous provinces worldwide, exemplified by the Norilsk sulfide-hosted platinum group element (PGE) deposits, part of the end-Permian Siberian Traps Magmatic Province. The high Pt concentration of the deposits here require multiple episodes of sulfide resorption and precipitation to concentrate the PGE elements, as well as assimilation of sulfate from country rocks to generate the heavy sulfur isotopic signature of the deposits (Li et al., 2009). Sediments at the Permian-Triassic boundary at many locations around the world show spikes in their metal concentrations, most notably in Ni (Rothman et al., 2014) but also other metals such as mercury (Sanei et al., 2012), which have been suggested to be linked to transport and deposition of volcanic gas/aerosols related to Siberian Traps volcanism. The direct observations of sulfide saturation in magmas, combined with the metal spikes in sediments, support the idea that sulfides played an important role in generating the gaseous outputs of LIPs in our geological past. Further studies to understand the interplay between sulfides and sulfur and metal degassing in present-day analogues will have clear implications in terms of understanding the economic and environmental implications for

these key events in the geological record as well as present-day global biogeochemical cycles and ore formation.

ACKNOWLEDGEMENTS

We acknowledge NERC urgency grant NE/M021130/1. The authors thank James Brenan, Michael Rowe and an anonymous reviewer for their helpful comments.

290 **References**

291 Berlo K, van Hinsberg V, Vigouroux N, Gagnon J, Williams-Jones A (2014) Sulfide breakdown
292 controls metal signature in volcanic gas at Kawah Ijen volcano, Indonesia. Chemical
293 Geology 371, 115-127.
294 Blake S, Self S, Sharma K, Sephton S (2010) Sulfur release from the Columbia River Basalts and
295 other flood lava eruptions constrained by a model of sulfide saturation. Earth and
296 Planetary Science Letters 299, 328-338.
297 Brenan JM (2015) Se–Te fractionation by sulfide–silicate melt partitioning: implications for the
298 composition of mantle-derived magmas and their melting residues. Earth and Planetary
299 Science Letters 422, 45-57.
300 Carroll M, Rutherford M (1985) Sulfide and sulfate saturation in hydrous silicate melts. Journal
301 of Geophysical Research: Solid Earth (1978–2012) 90, C601-C612.
302 Gauthier PJ, Sigmarsson O, Gouhier M, Haddadi B, Moune S (2016) Elevated gas flux and trace
303 metal degassing from the 2014‐2015 fissure eruption at the Bárðarbunga volcanic
304 system, Iceland. Journal of Geophysical Research: Solid Earth
305 Halter WE, Pettke T, Heinrich CA (2002) The origin of Cu/Au ratios in porphyry-type ore
306 deposits. Science 296, 1844-1846.
307 Jenner FE, O'Neill HSC (2012) Analysis of 60 elements in 616 ocean floor basaltic glasses.
308 Geochemistry, Geophysics, Geosystems 13,
309 Kiseeva ES, Wood BJ (2013) A simple model for chalcophile element partitioning between
310 sulphide and silicate liquids with geochemical applications. Earth and Planetary Science
311 Letters 383, 68-81.
312 Larocque AC, Stimac JA, Keith JD, Huminicki MA (2000) Evidence for open-system behavior in
313 immiscible Fe–S–O liquids in silicate magmas: implications for contributions of metals
314 and sulfur to ore-forming fluids. The Canadian Mineralogist 38, 1233-1249.
315 Li C, Ripley EM (2005) Empirical equations to predict the sulfur content of mafic magmas at
316 sulfide saturation and applications to magmatic sulfide deposits. Mineralium Deposita 40,
317 218-230.
318 Li C, Ripley EM, Naldrett AJ (2009) A new genetic model for the giant Ni-Cu-PGE sulfide
319 deposits associated with the Siberian flood basalts. Economic Geology 104, 291-301.
320 Liu Y, Samaha N-T, Baker DR (2007) Sulfur concentration at sulfide saturation (SCSS) in
321 magmatic silicate melts. Geochimica et Cosmochimica Acta 71, 1783-1799.
322 Masotta M, Keppler H, Chaudhari A (2016) Fluid-melt partitioning of sulfur in differentiated arc
323 magmas and the sulfur yield of explosive volcanic eruptions. Geochimica et
324 Cosmochimica Acta 176, 26-43.
325 Mather T, Witt M, Pyle D, Quayle B, Aiuppa A, Bagnato E, Martin R, Sims K, Edmonds M,
326 Sutton A (2012) Halogens and trace metal emissions from the ongoing 2008 summit
327 eruption of Kīlauea volcano, Hawaii. Geochimica et Cosmochimica Acta 83, 292-323.
328 Mavrogenes JA, O'Neill HSC (1999) The relative effects of pressure, temperature and oxygen
329 fugacity on the solubility of sulfide in mafic magmas. Geochimica et Cosmochimica Acta
330 63, 1173-1180.
331 Moune S, Sigmarsson O, Thordarson T, Gauthier P-J (2007) Recent volatile evolution in the
332 magmatic system of Hekla volcano, Iceland. Earth and Planetary Science Letters 255,
333 373-389.
334 Mungall JE, Brenan JM, Godel B, Barnes S, Gaillard F (2015) Transport of metals and sulphur in
335 magmas by flotation of sulphide melt on vapour bubbles. Nature Geoscience 8, 216-219.
336 Nadeau O, Williams-Jones AE, Stix J (2010) Sulphide magma as a source of metals in arc-related
337 magmatic hydrothermal ore fluids. Nature Geoscience 3, 501-505.
338 Parat F, Holtz F, Streck MJ (2011) Sulfur-bearing magmatic accessory minerals. Reviews in
339 Mineralogy and Geochemistry 73, 285-314.

340 Patten C, Barnes S-J, Mathez EA, Jenner FE (2013) Partition coefficients of chalcophile elements
341 between sulfide and silicate melts and the early crystallization history of sulfide liquid:
342 LA-ICP-MS analysis of MORB sulfide droplets. Chemical Geology 358, 170-188.
343 Ripley EM, Li C (2013) Sulfide saturation in mafic magmas: is external sulfur required for
344 magmatic Ni-Cu-(PGE) ore genesis? Economic Geology 108, 45-58.
345 Rothman DH, Fournier GP, French KL, Alm EJ, Boyle EA, Cao C, Summons RE (2014)
346 Methanogenic burst in the end-Permian carbon cycle. Proceedings of the National
347 Academy of Sciences 111, 5462-5467.
348 Sanei H, Grasby SE, Beauchamp B (2012) Latest Permian mercury anomalies. Geology 40, 63-
349 66.
350 Self S, Blake S, Sharma K, Widdowson M, Sephton S (2008) Sulfur and chlorine in Late
351 Cretaceous Deccan magmas and eruptive gas release. Science 319, 1654-1657.
352 Sigmarsson O, Haddadi B, Carn S, Moune S, Gudnason J, Yang K, Clarisse L (2013) The sulfur
353 budget of the 2011 Grímsvötn eruption, Iceland. Geophysical Research Letters 40, 6095-
354 6100.
355 Sigurdsson H, Devine J, Davis A (1985) The petrologic estimation of volcanic degassing. Jökull
356 1-8.
357 Thordarson T, Self S (1993) The Laki (Skaftár Fires) and Grímsvötn eruptions in 1783–1785.
358 Bulletin of Volcanology 55, 233-263.
359 Yang X-M (2012) Sulphur Solubility in Felsic Magmas: Implications for Genesis of Intrusion-
360 related Gold Mineralization. Geoscience Canada 39,
361 Zajacz Z, Candela PA, Piccoli PM, Sanchez-Valle C (2012) The partitioning of sulfur and
362 chlorine between andesite melts and magmatic volatiles and the exchange coefficients of
363 major cations. Geochimica et Cosmochimica Acta 89, 81-101.
364 Zajacz Z, Halter WE, Pettke T, Guillong M (2008) Determination of fluid/melt partition
365 coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions:
366 controls on element partitioning. Geochimica et Cosmochimica Acta 72, 2169-2197.
367

368 **LIST OF FIGURES**

369

370 **Figure 1**: Volcanic sulfides in basaltic tephra from Iceland and from Hawaii. a) backscattered
371 electron and (b) reflected light images of polished sections of Holuhraun tephra (erupted
372 November 2014 on the northern margin of the Vatnajokull ice cap, Iceland), showing basaltic
373 glass (gl), silicate minerals olivine (ol) and plagioclase (plg), bright sulfide globules and abundant
374 vesicles (v). c) a reflected light photomicrograph of an olivine crystal in tephra erupted during the
375 1959 eruption of Kīlauea Iki, Kīlauea Volcano, Hawaii, USA, containing inclusions of silicate
376 melt, vapor bubbles and spherical globules of quenched sulfide liquid. Images credited to
377 Margaret Hartley (a and b) and Isobel Sides (c).

378

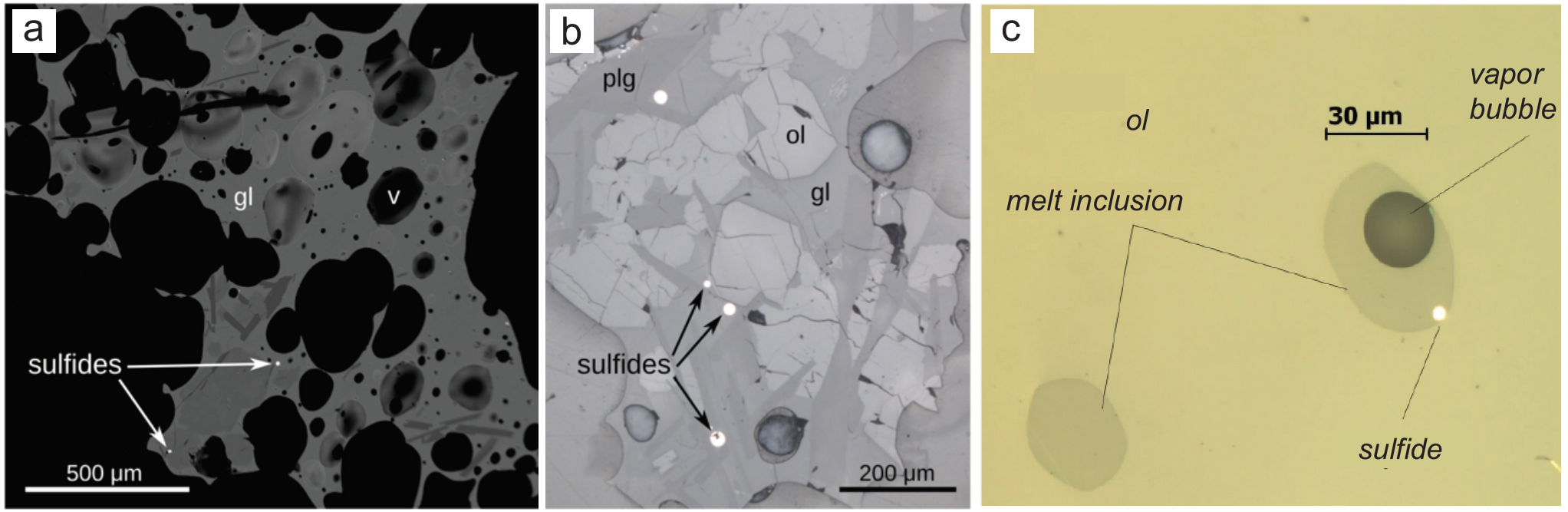
Figure 2: Schematic diagram to illustrate the primary processes of interest involving the interactions between magmatic sulfides and exsolved aqueous fluids in volcanic systems, and their implications for the formation of ore deposits, and/or outgassing of metals and sulfur to our atmosphere.

Figure 3: Sulfide saturation due to fractionational crystallization of initially sulfide-undersaturated mid-ocean ridge basaltic magma in the crust. Black curves show the sulfur concentration at sulfide saturation (SCSS) from (Li and Ripley, 2005). Grey curves on both plots show the concentration of sulfur rising as a result of fractional crystallization (assuming that sulfur behaves as an incompatible element). Two initial concentrations of sulfur are illustrated: 800 and 1100 ppm. Modified from (Li and Ripley, 2005) and (Ripley and Li, 2013).

Figure 4: Sketches to show the formation of monosulfide and intermediate sulfide solid solutions during cooling from magmatic temperatures; and the oxidation, decomposition and resorption of these sulfide phases in the presence of magmatic vapor bubbles in the melt. Abbreviations are: sl: sulfide liquid; mss: monosulfide solid solution; iss: intermediate solid solution; po: pyrrhotite; py: pyrite; cp: chalcopyrite. Magmatic iss and po destabilize relative to magnetite due to either changes in $f(O_2)$ and $f(S_2)$ and this leads to the release of metals from sulfides to the melt and/or magmatic fluids. These fluids are then either sequestered into ore bodies or, the case of volcanic systems, outgassed into the atmosphere. Modified from (Yang, 2012) and (Patten, et al., 2013).

Figure 5: The metal composition of volcanic plumes from Holuhraun (Iceland: (Gauthier, et al., 2016)) and Kīlauea (Hawaii: (Mather, et al., 2012)), analyzed using ICP-MS. The data are shown in units of the log of the enrichment factor (EF; by mass) relative to the element magnesium (Mg). Also shown are chalcophile element sulfide-silicate partition coefficients (Brenan, 2015,

404 Kiseeva and Wood, 2013), and aqueous fluid-melt partition coefficients (Zajacz et al., 2008)
405 plotted on top.
406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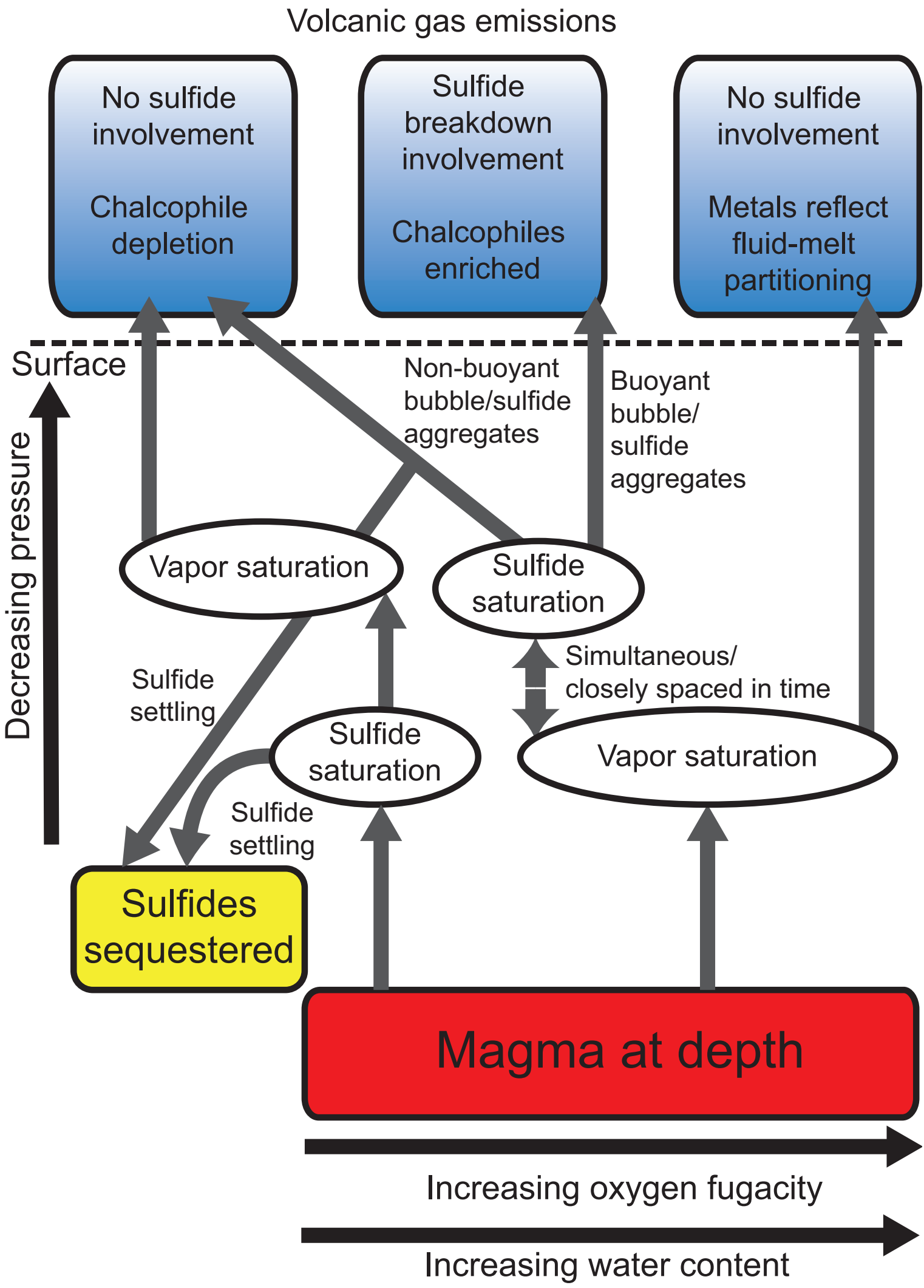
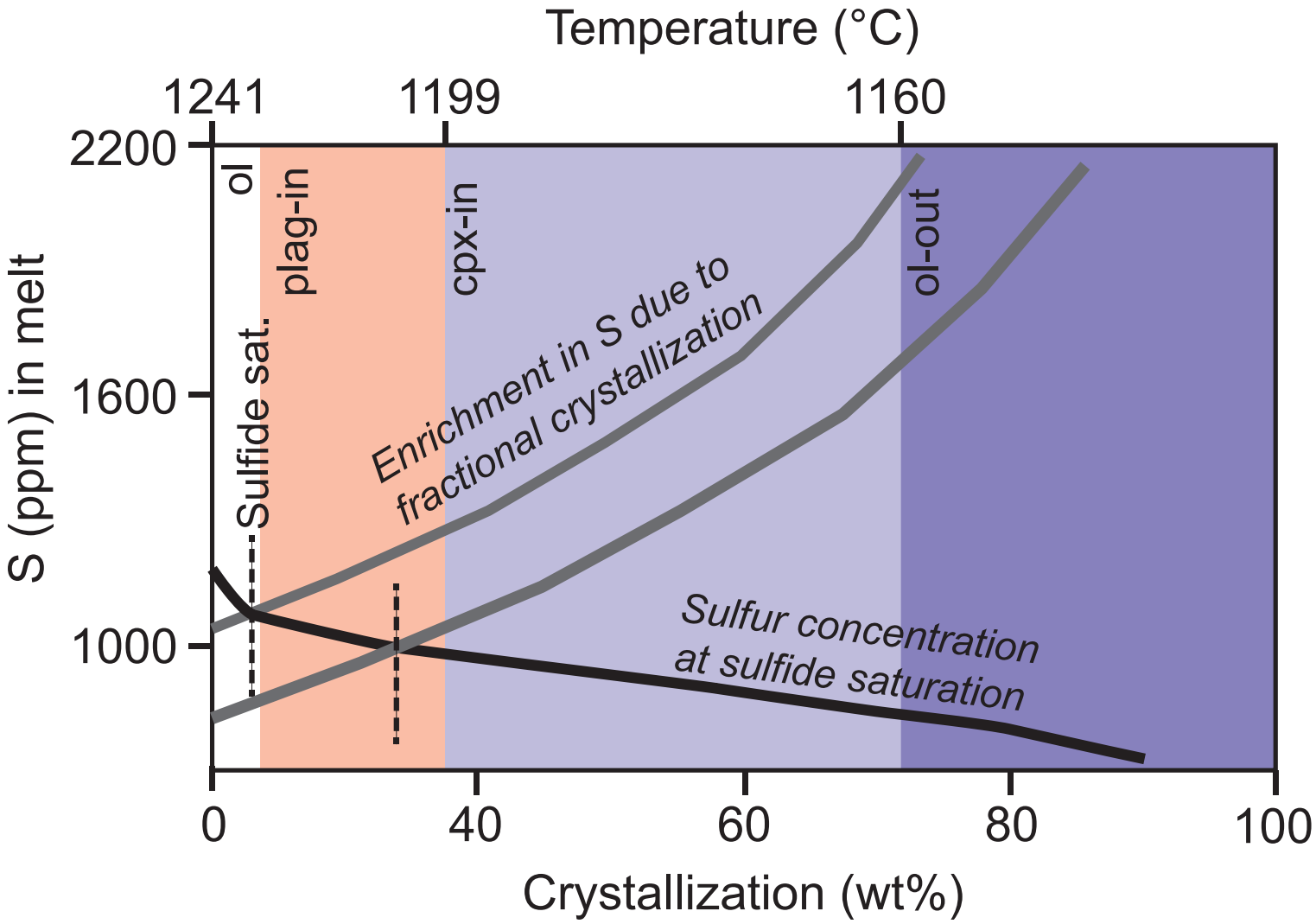
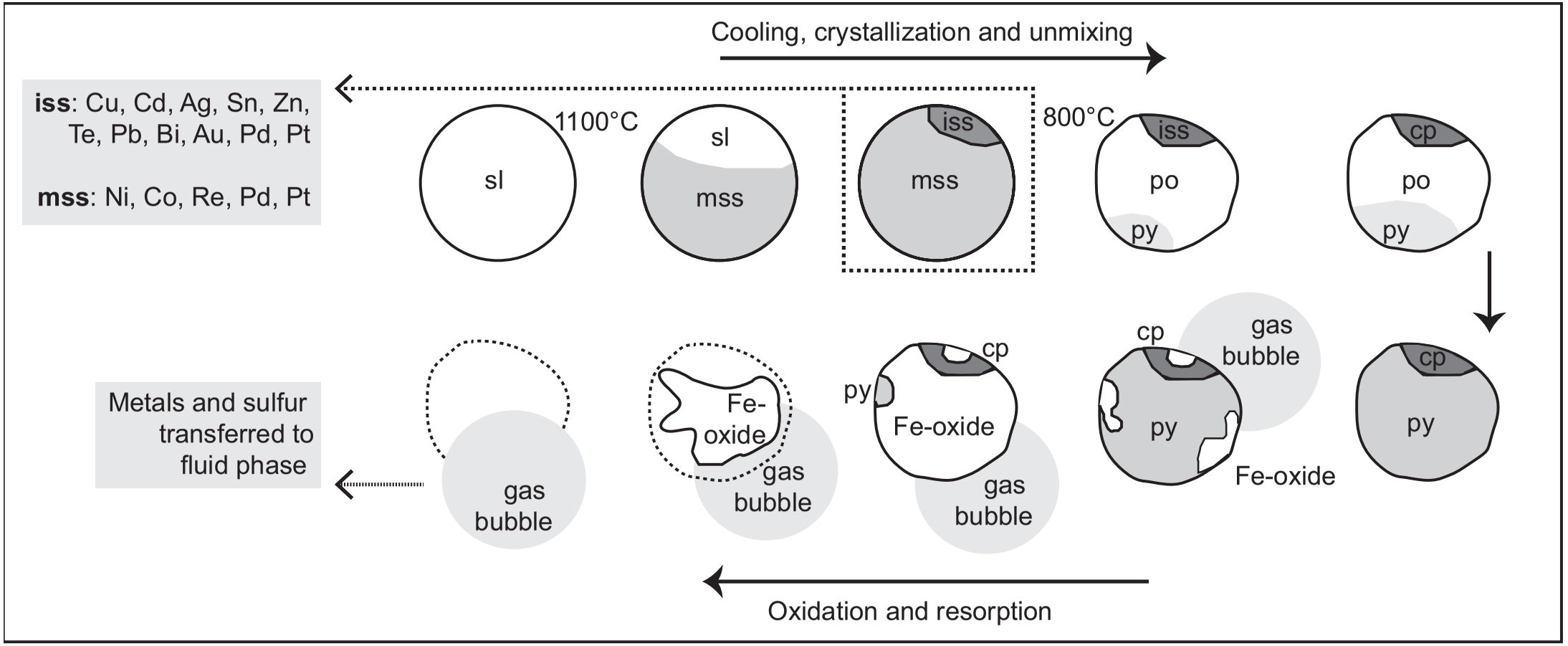
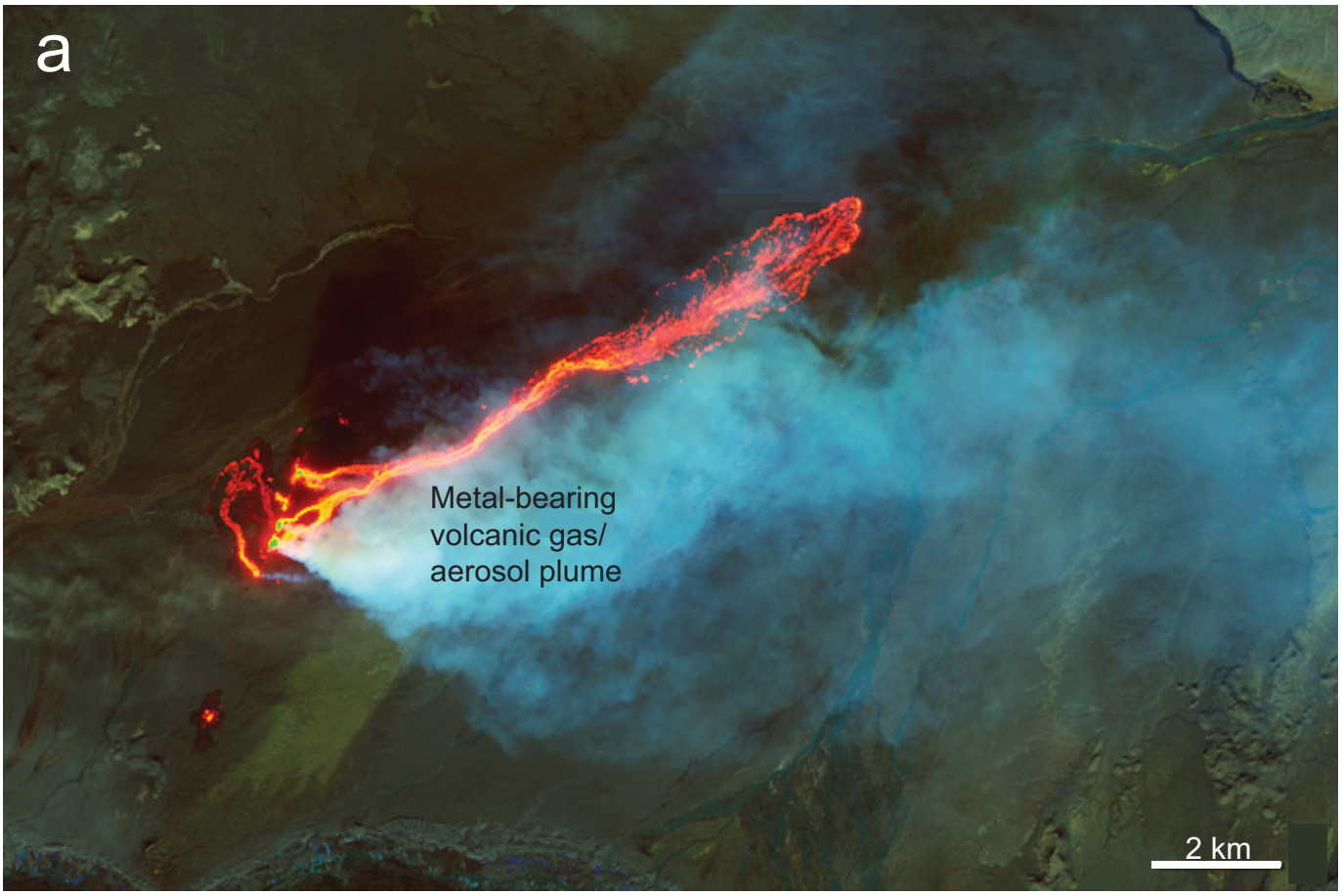

Volcanic gas emissions
No sulfide involvement
Chalcophile depletion
Sulfide breakdown involvement
Chalcophiles enriched
No sulfide involvement
Metals reflect fluid-melt partitioning
Surface
Decreasing pressure
Non-buoyant bubble/sulfide aggregates
Buoyant bubble/ sulfide aggregates
Vapor saturation
Sulfide saturation
Simultaneous/ closely spaced in time
Sulfide settling
Sulfide saturation
Vapor saturation
Sulfide settling
Sulfides sequestered
Magma at depth
Increasing oxygen fugacity
Increasing water content


Temperature (°C)
1241
1199
1160
2200
1600
1000
S (ppm) in melt
ol
plag-in
cpx-in
ol-out
Sulfide sat.
Enrichment in S due to fractional crystallization
Sulfur concentration at sulfide saturation
0
40
60
80
100
Crystallization (wt%)


Cooling, crystallization and unmixing
iss: Cu, Cd, Ag, Sn, Zn, Te, Pb, Bi, Au, Pd, Pt
mss: Ni, Co, Re, Pd, Pt
1100°C
sl
sl
mss
iss
mss
800°C
iss
po
py
cp
po
py
cp
py
cp
gas bubble
py
Fe-oxide
cp
py
Fe-oxide
gas bubble
Fe-oxide
gas bubble
gas bubble
Metals and sulfur transferred to fluid phase
Oxidation and resorption



Volcanic gas data

Holuhraun, Iceland

Kilauea, Hawaii

Sulfide-silicate melt partition coefficient

Aq. fluid-silicate melt partition coefficient